

10/673,613

Page 2

concentration range is specified for the DMTD additive. Wells indicates that the copper pyrophosphate bath with a DMTD-type additive yields bright and smooth deposits (column 1, lines 33-37) that are well-leveled (Claim 1), which, from our experience and the literature, can only be attained at DMTD concentrations well above 1 ppm (8 μM), for which the DMTD dimerizes in the plating bath to produce a dimer species that decelerates the copper deposition rate. This is consistent with the organic additive concentrations of 2.2 ppm and 5 ppm employed for the examples given by Wells (column 3, lines 44 and 64).

The inventors have discovered that a DMTD concentration below 0.5 ppm (4 μM) is required to give bottom up filling of small Damascene features. In this case, DMTD remains principally in the monomer form and does not produce the copper deposition rate suppression needed to provide the deposit brightening and leveling sought by Wells. However, the DMTD monomer (dominant at DMTD concentrations below 0.5 ppm) accelerates the copper deposition rate so as to provide bottom-up filling of Damascene features. Consequently, the Claims of the present application are currently being amended to limit the invention to use of the DMTD additive at concentrations below 4 μM (0.5 ppm) for plating of Damascene features.

Claims 1-6, 8-13, 16-19, 21-24, 26-28 and 30-32 were rejected under 35 U.S.C. 102(b) as being anticipated by Merricks et al. (U.S. Patent Application Publication 2002/0090484). The inventors acknowledge that the principal differences in the copper pyrophosphate bath of Merricks and that of the present invention are the intended use of the bath and the concentration of the 2,5-dimercapto-1,3,4-thiadiazole (DMTD) organic additive. Merricks claims use of the copper pyrophosphate bath only for repairing seed layers for the Damascene process (Paragraphs [0001] and [0010], and Claim 1), and specifies (Claim 10) use of a brightener additive at a concentration greater than 1.5 mg/L (corresponding to greater than 8 μM for DMTD). Note that Merricks is vague and inconsistent with respect to the brightener (DMTD) concentration, indicating an acceptable range from 0.1 to about 1000 ppm, and preferred ranges of 0.5 to 300 ppm, 1 to 100 ppm, and 2 to 50 ppm (paragraph [0028]) but specifying only <1 g/L for the examples (paragraphs [0045] and [0046]) and claiming >1.5 mg/L (Claim 10). In fact, for the

10/673,613

Page 3

Merrick's application of seed layer repair, the additive concentration is not critical since only a thin layer of copper conforming to the walls of the trenches and vias is deposited. For filling Damascene features using a copper pyrophosphate bath according to the present invention, the DMTD concentration is important, which distinguishes the present invention from the Merricks invention.

Merrick's mentions (paragraph [0036]) that an advantage of their invention is that the copper pyrophosphate bath can be used not only for seed layer enhancement but also to substantially metallize or fill the apertures with copper and thus also provide bottom-up fill or superfill. However, Merricks does not describe how bottom-up fill could be accomplished, and indeed uses an acid copper bath (Shipley ULTRAFILL 2001) for filling the Damascene features for both examples given (paragraphs [0045] and [0046]). Use of a copper pyrophosphate bath with a low concentration of DMTD to provide the copper electrodeposition acceleration needed for bottom-up filling of fine Damascene features was discovered by the present inventors and is novel with respect to the prior art.

Claim Rejections - 35 USC §103

Claims 7 and 15 were rejected under 35 USC 103(a) as being unpatentable over Merricks et al. in view of Shipley et al. (U.S. Patent 3,615,735). Claims 7 and 15 are dependent claims, adding further restrictions on the independent claims, and should be allowed if the independent claims on which they depend (Claims 1 and 10, respectively) are allowed. Claim 7 is currently cancelled.

Claims 14 and 29 were rejected under 35 USC 103(a) as being unpatentable over Merricks et al. in view of Jonker et al. (U.S. Patent 3,804,638). Claims 14 and 29 are dependent claims, adding further restrictions on other dependent claims, and should be allowed if the dependent claims on which they depend (Claims 13 and 28, respectively) are allowed.

Claims 20 and 33 were rejected under 35 USC 103(a) as being unpatentable over Merricks et al. in view of Wells et al. Claims 20 and 33 are dependent claims, adding further restrictions on

10/673,613

Page 4

the independent claims, and should be allowed if the independent claims on which they depend (Claims 10 and 26, respectively) are allowed.

Claim 25 was rejected under 35 USC 103(a) as being unpatentable over Merricks et al. in view of Wells et al. and Jonker et al. Claim 25 is analogous to Claim 10 but contains additional limitations. Claim 25 should be allowed if Claim 10 is allowed.

AMENDMENTS

Claim Amendments

The Claims are currently amended as follows:

Claims 1-9, 16, and 21-23 are cancelled.

Claim 10 is amended such that the bath constituent "an organic additive compound that tends to accelerate the copper electrodeposition rate" is replaced by "2,5-dimercapto-1,3,4-thiadiazole at a concentration of less than 4 μM ", and the limitation "whereby copper metal is electrodeposited in Damascene trenches and vias to form circuitry on semiconductor chips" is added.

Claims 24, 25 and 26 are amended to limit the concentration range for 2,5-dimercapto-1,3,4-thiadiazole to less than 4 μM by replacing "in the range from 1 to 5 μM " with "of less than 4 μM ".

These amendments effectively limit the invention to use of a copper pyrophosphate bath containing less than 4 μM of the DMTD additive for depositing copper in Damascene trenches and vias to form circuitry on semiconductor chips. Support for the "less than" terminology is found in the original specification (page 9, lines 7-9).